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Development of D–π–A dye with benzothienopyridine as electron-withdrawing anchoring group for dye-sensitized solar cells

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D–π–A dye SAT-1 with benzo[4,5]thieno[2,3-c]pyridine as electron-withdrawing anchoring group capable of forming a hydrogen bonding at the Brønsted acid sites or a coordinate bonding at the Lewis acid sites on TiO₂ surface has been developed as a new-type of D–π–A dye sensitizer for dye-sensitized solar cells.

Dye-sensitized solar cells (DSSCs) based on dye sensitizers adsorbed on nanocrystalline TiO₂ electrodes are of considerable scientific and practical interest from the viewpoint of their interesting construction and operational principles, colorful and decorative nature, and low cost of production. To develop high-performance DSSCs, many kinds of donor-acceptor π-conjugated (D–π–A) dyes possessing both electron-donating (D) and electron-withdrawing anchoring (A) groups linked by π-conjugated bridges, possessing broad and intense absorption spectral features, have been designed and developed so far, and would be especially expected to be one of the most promising classes of organic dye sensitizers. Recently, to create more effective D–π–A dye sensitizers, many researchers focused on the design and synthesis of new types of D–π–A dye sensitizers with electron-withdrawing anchoring groups such as the nitro group, aldehyde, and 2-(1,1-dicyanomethylene)rhodanine, pyridine, and 8-hydroxyquinoline as an alternative to conventional carboxyl groups. In our previous work, we found that a new type of D–π–A dye sensitizers can inject electrons efficiently from the pyridyl group to the conduction band (CB) of the TiO₂ electrode through coordinate bonding, rather than the bidentate bridging linkage between conventional D–π–A dye sensitizers with carboxyl groups and the Brønsted acid sites (surface-bound hydroxyl groups, Ti–OH) on TiO₂ surface. More recently, we have found that the D–π–A dye sensitizer with two pyridyl groups is predominantly adsorbed on the TiO₂ surface through hydrogen bonding at Brønsted acid sites. In addition, the photovoltaic performances of DSSCs based on D–D–π–A organic dyes and a series of porphyrin-based dyes with pyridyl groups were reported by Zheng et al. and Coutsolelos et al., respectively. However, to provide a direction in molecular design toward creating efficient D–π–A dye sensitizers with pyridyl groups, further fundamental studies to obtain useful knowledge about not only the bonding mode of the dyes on the TiO₂ surface but also the influences of the bonding modes on the photovoltaic performances of DSSCs are therefore necessary.

Therefore, in this work, we have designed and synthesized D–π–A dye SAT-1 with thiophene-fused pyridine ring, benzo[4,5]thieno[2,3-c]pyridine as electron-withdrawing anchoring group (Scheme 1), as an alternative to conventional carboxyl groups. In addition, to investigate the influences of substituent on the bonding mode of benzo[4,5]thieno[2,3-c]pyridine derivatives, we have synthesized BTP-H without a substituent, BTP-CI with chloride atom as an electron-withdrawing substituent and BTP-T with a thiophene ring as an electron-donating substituent. It was found the dye SAT-1 is predominantly adsorbed on the TiO₂ surface through the hydrogen bonding at Brønsted acid sites, whereas the benzo[4,5]thieno[2,3-c]pyridine derivatives are predominantly adsorbed on the TiO₂ surface through coordinate bonding at Lewis acid sites. Here, we reveal the influences of interaction between the pyridyl group of the dye and TiO₂ surface on the photovoltaic performances of SAT-1.

The absorption and fluorescence spectra of SAT-1 in THF are shown in Fig. 1a. A strong absorption band with absorption peak wavelength at 408 nm is assigned to the intramolecular charge transfer (ICT) excitation from the electron donor moiety (triphenylamine) to the electron acceptor moiety (benzothienopyridine). The molar extinction coefficient (ε) for the ICT band is 56400 M⁻¹ cm⁻¹. The corresponding fluorescence maximum (λ_{flu}) occurs at 500 nm, and the fluorescence quantum yield (Φ_flu) is 0.80. The MO
calculations (AM1, INDO/S) indicate that the longest excitation band is mainly attributable to the transition from the HOMO to the LUMO, where the HOMO is mostly localized on the triphenylamine moiety containing a thiophene ring, and the LUMO is mostly localized on the benzothienoypyridine moiety containing a thiophene ring (Figs. 2a, b). The changes in the calculated electron density accompanied by the first electronic excitations for SAT-I reveal a strong ICT nature from the triphenylamine moiety to the benzothienoypyridine moiety upon photoexcitation (Fig. 2c).

On the other hand, the absorption band of SAT-I adsorbed on the TiO2 film is broadened compared with that in 1,4-dioxane (Fig. 1b). However, the absorption peak wavelength of SAT-I adsorbed on TiO2 is similar to that in 1,4-dioxane. Thus, this result indicates that SAT-I forms weak π-stacked aggregates on TiO2 surface, which has little influence on the absorption spectrum of the dyes adsorbed on TiO2 surface.

Thus, to elucidate the adsorption states of SAT-I, BTP-H, BTP-Cl and BTP-T on TiO2 nanoparticles, we measured the FTIR spectra of the powders and the compounds adsorbed on TiO2 nanoparticles (Fig. 3). For the powders of SAT-I and the three derivatives, the characteristic stretching bands for C=N or C=C were clearly observed at around 1595 cm⁻¹. In the FTIR spectra of BTP-H, BTP-Cl and BTP-T adsorbed on TiO2 nanoparticles, the band at around 1595 cm⁻¹ disappeared completely, and a new and strong band appeared at 1606 cm⁻¹ for BTP-H, 1602 cm⁻¹ for BTP-Cl and 1601 cm⁻¹ for BTP-T, respectively, which can be assigned to the coordinated pyridyl group to the Lewis acid sites on the TiO2 surface. These observations clearly indicate that BTP-H, BTP-Cl and BTP-T are predominantly adsorbed on the TiO2 surface through coordinate bonding at Lewis acid sites, whereas the dye SAT-I is predominantly adsorbed on the TiO2 surface through the hydrogen bonding at Brønsted acid sites (Fig. 4).

Interestingly, when the dye SAT-I was adsorbed on the TiO2 nanoparticles, the stretching band at 1594 cm⁻¹ is shifted by 4 cm⁻¹ to higher wavenumber, that is, the band at 1598 cm⁻¹ can be assigned to the hydrogen-bonded pyridyl group to Brønsted acid sites on the TiO2 surface. These results reveal that the formation of coordinate bonding or hydrogen bonding between the pyridyl group of dye and the TiO2 surface can be controlled by adjusting the electron density on the nitrogen atom of the pyridyl group. Further studies to ensure this conclusion are now in progress by estimating pKa values of SAT-I and the benzo[4,5]thieno[2,3-c]pyridine derivatives and will be reported in a subsequent paper.
fluorescence spectra (458 nm; 2.71 eV). The LUMO energy level for the dye was –1.84 V, which is higher than the energy level of the CB of TiO$_2$ (–0.5 V), so that the dye SAT-1 can efficiently inject electrons to the TiO$_2$ electrode.

The arrow denotes the direction of the potential scan.

![Cyclic voltammogram of SAT-1 in acetonitrile containing 0.1 M Bu$_4$NClO$_4$ at a scan rate of 100 mV s$^{-1}$.](image)

The DSSC was prepared using the dye-adsorbed TiO$_2$ electrode (9 μm), Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as an electrolyte. The photocurrent–voltage ($I$–$V$) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm$^{-2}$). The incident photon-to-current conversion efficiency (IPCE) spectrum and the $I$–$V$ curve are shown in Fig. 6. It is worth mentioning here that the adsorption amount of SAT-1 adsorbed on TiO$_2$ electrode is $9.5 \times 10^{16}$ molecules per cm$^2$, which is comparable to that of conventional D–π–A dye sensitizers with carboxyl groups.

The DSSC based on SAT-1 gave a solar energy-to-electricity conversion yield ($\eta$) of 1.11% with a short-circuit photocurrent density ($J_{sc}$) of 3.12 mA cm$^{-2}$, a fill factor ($\eta$) of 0.548 mV, and an open-circuit voltage ($V_{oc}$) of 0.67, which is comparable to that of conventional D–π–A dye sensitizers with carboxyl groups.

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**Notes and references**

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